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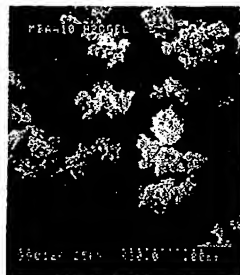
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80058 München (DE)**(54) **Water-swella-ble crosslinked polymer, its composition, and their production processes and uses**

(57) The present invention provides a water-swella-ble crosslinked polymer composition which comprises an anionic crosslinked polymer and a cationic crosslinked polymer, and is excellent in the desalting property and further in the absorption properties under load, and is therefore highly practicable. In a water-swella-ble crosslinked polymer composition which is particulate and comprises a cationic crosslinked polymer and an anionic crosslinked polymer, the improvement satisfies the following requirements (1) and/or (2):

(1) At least either one of the cationic crosslinked polymer and the anionic crosslinked polymer has a bulk density of not more than 0.5 g/ml.

(2) The water-swella-ble crosslinked polymer composition has a bulk density of not more than 0.5 g/ml.

Fig. 1

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## Description

## BACKGROUND OF THE INVENTION

## A. TECHNICAL FIELD

[0001] The present invention relates to a water-swella-ble crosslinked polymer composition and its production process, more specifically, a water-swella-ble crosslinked polymer composition and its production process wherein the water-swella-ble crosslinked polymer composition comprises an anionic crosslinked polymer and a cationic crosslinked polymer and has a bulk density in a specific range. The present invention further relates to a water-swella-ble crosslinked polymer and its production process wherein the water-swella-ble crosslinked polymer is to easily give the above water-swella-ble crosslinked polymer composition. The present invention still further relates to uses of the above water-swella-ble crosslinked polymer composition.

## B. BACKGROUND ART

[0002] In recent years, synthetic water-absorbing materials, which are called water-absorbent resins, have been developed and are being put to practical use not only as constituent materials of sanitary materials such as sanitary napkins and disposable diapers, but also for purposes which need the water-absorbent resin, for example, industrial purposes such as sealing materials, dewfall-preventive materials, freshness-keeping materials, and solvent-dehydrating materials, and water-holding purposes in such as tree planting, agriculture, and horticulture.

[0003] As to the above water-absorbent resin, many ones are obtained by giving a crosslinked structure to hydrophilic high-molecular compounds are known, and examples thereof include: partially-neutralized and crosslinked poly(acrylic acids); hydrolyzed graft polymers of starch-acrylonitrile; neutralized graft polymers of starch-acrylic acid; saponified copolymers of vinyl acetate-acrylic acid ester; hydrolyzed copolymers of acrylonitrile or acrylamide, or crosslinked polymers of these hydrolyzed copolymers; and crosslinked polymers of polyethylenimine.

[0004] Furthermore, WO 92/20735 discloses a technical fundamental conception about absorption of electrolyte solutions by combinations of polymer particles having two different ions and exhibiting the ion exchangeability, and examples of application of this technique are disclosed in JP-A-081468/1992, WO 98/24382, WO 98/37149, and WO 99/25393. These techniques are, for example, such that an anionic water-swella-ble crosslinked polymer particle is combined with a cationic water-swella-ble crosslinked polymer particle to form a neutralized structure from an acid group of the former polymer particle and a basic group of the latter polymer particle by the salts which absorb solutions contain, with the result that each of these polymer particles becomes a water-swella-ble that the combination of these polymer particles can exhibit more excellent swellability than conventional neutralized water-absorbent resins, and further can also take electrolytes (which are a problem to the conventional neutralized water-absorbent resins) into prevent the salt effect and, as a result, can enhance the ability to absorb the electrolyte solutions much more than conventional cases.

[0005] However, the above WO 92/20735, WO 98/24382, and WO 98/37149 merely disclose technical fundamental conceptions about combinations of polymer particles, and never consider absorption properties in practical use. In addition, WO 99/25393 proposes forming a microdomain in the polymer particles for the purpose of improving the absorption properties, but this case is found to contrarily deteriorate the desalting effect. The efficiency in the use of water-absorbing materials is important particularly for practical use of such as disposable diapers, therefore the diffusibility of liquids and further the properties of absorbing the electrolyte solution are more important; nevertheless this respect is not taken into consideration in the above prior arts at all. Thus, in the case where the above prior arts are intactly applied to such as disposable diapers, there are problems in respect to such as absorption rate, absorption capacity, and liquid permeability, therefore as satisfactory product is not obtained.

## SUMMARY OF THE INVENTION

## A. OBJECTS OF THE INVENTION

[0006] An object of the present invention is to provide a water-swella-ble crosslinked polymer composition and its production process wherein the water-swella-ble crosslinked polymer composition comprises an anionic crosslinked polymer and a cationic crosslinked polymer, and is excellent in the desalting property and further in the absorption properties under load, and is therefore highly practicable. Another object of the present invention is to provide: a water-swella-ble crosslinked polymer and its production process wherein the water-swella-ble crosslinked polymer is to easily give the above water-swella-ble crosslinked polymer composition; and further, uses of the above water-swella-ble crosslinked polymer composition.

**B. DISCLOSURE OF THE INVENTION**

[0007] In order to solve the above problems, the present invention provides the following:

- (1) A water-swellaible crosslinked polymer composition, which is particulate and comprises an anionic crosslinked polymer and a cationic crosslinked polymer, with the water-swellaible crosslinked polymer composition being characterized by having a bulk density of not more than 0.5g/ml.
- (2) A water-swellaible crosslinked polymer composition, which is particulate and comprises an anionic crosslinked polymer and a cationic crosslinked polymer, with the water-swellaible crosslinked polymer composition being characterized in that at least either one of the anionic crosslinked polymer and the cationic crosslinked polymer has a bulk density of not more than 0.5g/ml.
- (3) A particulate cationic crosslinked polymer, which has a bulk density of not more than 0.5g/ml and exhibits an absorption capacity of at least 5g/g for physiological saline solution without load.
- (4) A production process for a water-swellaible crosslinked polymer, which comprises the step of carrying out a crosslinking reaction of a solution under bubbles-containing conditions wherein the solution contains at least a water-soluble polymer and a crosslinking agent.
- (5) A production process for a water-swellaible crosslinked polymer composition, which comprises the steps of: carrying out a crosslinking reaction of a solution under bubbles-containing conditions to obtain a cationic crosslinked polymer wherein the solution contains at least a polyamine and a crosslinking agent, and then mixing the resultant cationic crosslinked polymer and an anionic crosslinked polymer together.
- (6) An absorbent articles, which comprises an absorbent layer, a sheet with liquid permeability, and a sheet with liquid impermeability, wherein the absorbent layer contains the above water-swellaible crosslinked polymer composition according to the present invention, and is interposed between the sheet with liquid permeability and the sheet with liquid impermeability.

[0008] These and other objects and the advantages of the present invention will be more fully apparent from the following detailed disclosure.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0009]

Fig. 1 is an electron photomicrograph (magnifications: 30.0) of the crosslinked polymer particles (A3) as obtained in Example A-3.

Fig. 2 is an electron photomicrograph (magnifications: 30.0) of the crosslinked polymer particles (A5) as obtained in Comparative Example A-2.

Fig. 3 shows the absorption capacities under load in 4 hours of the water-swellaible crosslinked polymer compositions (1) to (8) as obtained in Examples 1 to 4 and Comparative Examples 1 to 4.

Fig. 4 shows the absorption capacities under load in 20 hours of the water-swellaible crosslinked polymer compositions (1) to (8) as obtained in Examples 1 to 4 and Comparative Examples 1 to 4.

**DETAILED DESCRIPTION OF THE INVENTION**

[0010] The water-swellaible crosslinked polymer composition, according to the present invention, comprises a cationic crosslinked polymer and an anionic crosslinked polymer, and satisfies the following requirements (1) and/or (2):

(1) At least either one of the cationic crosslinked polymer and the anionic crosslinked polymer has a bulk density of not more than 0.5g/ml, preferably not more than 0.4g/ml.

(2) The water-swellaible crosslinked polymer composition has a bulk density of not more than 0.5g/ml, preferably not more than 0.4g/ml.

[0011] Incidentally, the "bulk density" in the present invention is a mass per unit volume of a sample, and has the same meaning as those of common terms such as apparent density and bulk specific gravity. In the present invention, the measurement of the "bulk density" is carried out in accordance with the Japanese Industrial Standard (JIS) K3362 8.2.

[0012] The reduction of the bulk density to the above small value enlarges the surface area of the particles, therefore the desalination and the neutralization rapidly occur due to the ion exchange by the cationic crosslinked polymer and the anionic crosslinked polymer, with the result that the absorption rate under load is enhanced. In addition, the

above low bulk density enhances the liquid permeability in the initial stage of the water absorption and, as a result, also enhances the saturated absorption capacity value (absorption quantity). Just for the purpose of enlarging the surface area, it is enough to render the particle diameter small. However, just to simply render the particle diameter small involves enhancing the bulk density and therefore deteriorating the liquid permeability. In addition, in the above prior art as disclosed in WO92/20735, JP-A-081468/1992, WO98/24382, and WO98/37149, irregular pulverized polymer particles are combined with each other. Furthermore, in the above prior art as disclosed in WO99/25393, kneading is repeated with an extruder until the micro domain is formed. Thus, any polymer particle is resultant from these prior arts has a bulk density of more than 0.5g/ml.

[0013] Thus, the present inventors found that, in the present invention, both the fast liquid permeation rate and the fast absorption rate under load can be achieved by using the cationic or anionic crosslinked polymer having a small bulk density and a large surface area or the composition comprising a mixture of these crosslinked polymers.

[0014] The cationic crosslinked polymer, as used in the present invention, is preferably such that 50 to 100 mol% of basic groups which are contained in functional groups in molecules of this polymer are unneutralized basic groups, and examples thereof include those which are crosslinked slightly to such an extent that they can exhibit the water-swelling ability and be water-insoluble, specifically, crosslinked polymers of polyalkyleneamines, crosslinked polymers of polyvinylamines, crosslinked polymers of polyallyl amines, crosslinked polymers of poly(N-vinylimidazoles), crosslinked polymers of polyvinylpyridines, crosslinked polymers of poly(vinylpyridine amine oxides), crosslinked polymers of polydiallyl amines, crosslinked polymers of polyamide polyamines, crosslinked polymers of poly(dimethylaminoalkyl acrylates), crosslinked polymers of poly(dimethylaminoalkyl methacrylates), crosslinked polymers of polydimethylaminoalkyl acrylamides, crosslinked polymers of polydimethylaminoalkyl methacrylamides, crosslinked polymers of polyamides, crosslinked polymers of poly(hydrazine acrylic acids), crosslinked polymers of asparagic acid-hexamethylenediamine polycondensation products, crosslinked polymers of basic poly(amino acids) (e.g. polylysine), crosslinked polymers of chitosan, and copolymers of these polymers. Among them, particularly preferable ones are crosslinked polymers of polyethylenimines, crosslinked polymers of polyallyl amines, and their derivatives, and especially preferable ones are the crosslinked polymers of polyethylenimines.

[0015] The cationic crosslinked polymer, as used in the present invention, is obtainable by a process including the step of crosslinking the corresponding cationic polymer with a crosslinking agent having at least two groups which are to react with a functional group (e.g. amino (amine) group) of the cationic polymer to thereby form a covalent bond, thus introducing a crosslinked structure into the cationic polymer. When the above functional group of the cationic polymer is an amino (amine) group, usable examples of the crosslinking agent include conventional compounds which have, per molecule, at least two groups such as epoxy groups, aldehyde groups, haloalkyl groups, isocyanate groups, carboxyl groups, acid anhydride groups, acid halide groups, ester bonding moieties, and activated double bonds. Specific examples of such a crosslinking agent include: bisepoxy compounds; epichlorohydrin; dihalides such as dibromoethylene, formalin; dialdehyde compounds such as glyoxal; diglycidyl ethers of (poly)ethylene glycols, diglycidyl ethers of (poly)propylene glycols, diglycidyl ethers of (poly)tetrahydrofuran glycols, diglycidyl ethers of glycerol;  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid esters such as methyl acrylate and ethyl acrylate;  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids such as acrylic acid; di- $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds such as N,N'-methylene bisacrylamide; and  $\alpha$ ,  $\omega$ -alkylenedil isocyanates. However, there is no limitation thereto. The kind and the amount of the crosslinking agent are selected in view of factors such as absorption capacity or strength of the resultant cationic crosslinked polymer, but, when the cationic polymer is a polymer containing an amino (amine) group, the amount of the crosslinking agent is preferably in the range of 0.001 to 20 mol% of the amine units of the polymer. In the case where the amount of the crosslinking agent is smaller than 0.001 mol%, the absorption capacity of the resultant cationic crosslinked polymer is low, and further, its strength is insufficient. In the case where the amount of the crosslinking agent is larger than 20 mol%, the absorption capacity might greatly be lowered.

[0016] The crosslinked polymer of polyethylenimine is producible by a process including the step of crosslinking a polymer of polyethylenimine which is in a state diluted with a solvent to form a aqueous solution or in a solvent-free state. However, for the safety, it is preferable that the polymer of polyethylenimine which is in a state of a aqueous solution is crosslinked. In addition, for preventing the physical properties from deteriorating due to drying after crosslinking, or for simplifying the drying step, it is desirable to produce a polymer of polyethylenimine having a high solid content, and the solid content of the polymer of polyethylenimine which is in a state of a aqueous solution is preferably not lower than 80 weight%, more preferably not lower than 90 weight%, most preferably not lower than 95 weight%.

[0017] The anionic crosslinked polymer, as used in the present invention, is preferably such that 50 to 100 mol% of acid groups which are contained in functional groups in molecules of this polymer are unneutralized acid groups, and examples thereof include those which are crosslinked slightly to such an extent that they can exhibit the water-swelling ability and be water-insoluble, specifically, homopolymer of acid-group-containing polymerizable monomers, such as crosslinked polymers of poly(acrylic acids). Examples of the acid-group-containing polymerizable monomers include: carboxyl-group-containing polymerizable monomers such as acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, sorbic acid, maleic acid, itaconic acid, cinnamic acid, and their anhydrides; sulfonic acid-group-containing

polymerizable monomers such as vinylsulfonic acid, allylsulfonic acid, styrenesulfonic acid, vinyltoluenesulfonic acid, 2-(meth)acrylamido-2-methylpropanesulfonic acid, 2-(meth)acryloylethanesulfonic acid, and 2-(meth)acryloylpropanesulfonic acid; and phosphoric acid-group-containing polymerizable monomers such as 2-hydroxyethylacryloylphosphate, 2-hydroxyethylmethacryloylphosphate, phenyl-2-acryloyloxyethylphosphate, and vinylphosphate. Among them, particularly preferable ones are crosslinked polymers of poly(acrylic acids), crosslinked polymers of poly(maleic acids), and their derivatives.

[0018] In the present invention, the cationic crosslinked polymer and the anionic crosslinked polymer are used in a form where preferably at least 70 mol%, more preferably 100 mol%, of the acid or basic groups of each polymer are unneutralized and free.

[0019] For requirement (1) above, it is enough that at least either one of the cationic crosslinked polymer and the anionic crosslinked polymer has a bulk density of not more than 0.5 g/ml, and this includes the following three cases:

- (i) a case where both of the cationic crosslinked polymer and the anionic crosslinked polymer have a bulk density of not more than 0.5 g/ml;
- (ii) a case where the cationic crosslinked polymer has a bulk density of not more than 0.5 g/ml and where the anionic crosslinked polymer has a bulk density of more than 0.5 g/ml; and
- (iii) a case where the anionic crosslinked polymer has a bulk density of not more than 0.5 g/ml and where the cationic crosslinked polymer has a bulk density of more than 0.5 g/ml.

In view of the ease of the production, however, it is preferable that the cationic crosslinked polymer has a bulk density of not more than 0.5 g/ml, and case (ii) above is the simplest. Particularly, it is preferable that particles of crosslinked polymers of polyethylenimine having a bulk density of not more than 0.5 g/ml are used as the cationic crosslinked polymer.

[0020] The crosslinked polymer of polyethylenimine has a low glass transition temperature and is very difficult to subject to treatments such as pulverization at room temperature after drying. Therefore, special treatments such as freeze-drying are needed for obtaining its irregular pulverized particles. In addition, even if the pulverization is carried out by such special treatment, the resultant particles tend to cohere if they are left as they are. Therefore, usually, their surfaces need to be coated with inorganic fine particles such as silica. On the other hand, the crosslinked polymer of polyethylenimine can be formed into aggregated particles having a bulk density in the aimed range by subjecting the crosslinked polymer of polyethylenimine to a process including the steps of pulverizing the crosslinked polymer of polyethylenimine before and in the stage of its hydrogel to divide it into very fine pieces (e.g. their particle diameters are not larger than 850  $\mu\text{m}$ ), and then drying them, and then adding thereto a small amount of inorganic fine particles (such as silica) or surfactant, and then pulverizing the resultant mixture. The resultant aggregate usually has a bulk density of not more than 0.5 g/ml, therefore crosslinked polymer particles having a bulk density of not more than 0.5 g/ml are obtainable in a very economical and practical manner.

[0021] Examples of other production processes for cationic or anionic crosslinked polymer particles having a bulk density of not more than 0.5 g/ml include a process including the steps of carrying out a reaction of a solution under bubbles-containing conditions where in the solution contains a water-soluble polymer and a crosslinking agent, and more specifically examples of such a process include: a process including the steps of beforehand adding a compound, which can generate gas by heating, to a cationic or anionic water-soluble polymer along with a crosslinking agent, and then heating the resultant mixture to cause foaming simultaneously with crosslinking, thus obtaining a crosslinked polymer having a low density; and a process including the steps of crosslinking a mixture of a cationic or anionic water-soluble polymer or a cationic or anionic polymerizable monomer containing a polymerization initiator with a crosslinkable compound in an aqueous solution of this mixture in a state where an inert gas is dispersed in this aqueous solution, or crosslinking the above mixture simultaneously with its polymerization, thus obtaining a crosslinked polymer having a low density.

[0022] The process including the steps of carrying out a reaction between a water-soluble polymer and a crosslinking agent under bubbles-containing conditions may be the above-exemplified ones, but a particularly preferable example thereof is a process including the step of carrying out a crosslinking reaction between a viscous water-soluble polymer and a crosslinking agent under bubbles-containing conditions, because, also in view of the production cost, such a process enables the stable production at a low cost. For stabilizing the bubbles-containing conditions in this process, it is desirable to control the viscosity, and this viscosity control is, for example, carried out by a method in which the molecular weight, molecular composition, or high-molecular structure of the water-soluble polymer is controlled, or a method in which the temperature or pressure is adjusted, or a method in which an additive is added. However, a method in which the solid content of the aqueous solution is adjusted is preferable as a simple method, wherein how high the solid content is preferable is different according to the viscosity of the polymer solution, but the solid content is preferably not lower than 5 weight%, more preferably not lower than 30 weight%, still more preferably not lower than 50 weight%, most preferably not lower than 80 weight%. In the case where the solid content is lower than 5 weight%,

there are disadvantages in that they yield resultant from drying is slow. The viscosity of the polymer solution is preferably not lower than 2 mPa s, more preferably not lower than 100 mPa s, still more preferably not lower than 1,000 mPa s, most preferably not lower than 10,000 mPa s. The weight-average molecular weight of the polymer which is contained in the polymer solution is preferably not lower than 1,000, more preferably not lower than 10,000, most preferably not lower than 1,000,000. The neutralization ratio of the polymer which is contained in the polymer solution is preferably lower than 75 mol%, more preferably lower than 50 mol%, still more preferably lower than 30 mol%, most preferably lower than 10 mol%. The degree of reduced pressure in the above method in which the pressure is adjusted is preferably not higher than 750 mmHg, more preferably not higher than 200 mmHg, most preferably not higher than 100 mmHg. The volume expansivity of the bubbles-containing volume to the original volume is preferably not lower than 0.1 % more preferably not lower than 0.5%, still more preferably not lower than 10%, most preferably not lower than 50%.

[0023] The mixer, which is used to mix the water-soluble polymer and the crosslinking agent together while whipping them, is not especially limited, but conventional ones such as motor-driven rotating stirrers, high-speed stirrers (e.g. homogenizers (produced by Nihonseiki Kaisha Ltd.)), and whisks (e.g. Whip Auto (produced by Aikosha Seisakusho K. K.)) are also usable according to the aimed bulk density. In addition, the pressure upon the whipped aqueous polymer solution can be adjusted as a method to adjust the bulk density of the crosslinked polymer. For example, crosslinking the crosslinking-agent-mixed aqueous polymer solution under reduced pressure after being whipped can produce any crosslinked polymer having a lower bulk density than that obtained by crosslinking under normal pressure. In addition, uniform whipping enables easy pulverization of even a high-concentrated crosslinked polymer.

[0024] The crosslinked hydrogel polymer as produced in the above way is used after it has been dried and then pulverized if necessary.

[0025] The present inventors are the first finders of the above production process for a water-swellaable crosslinked polymer which comprises the step of carrying out a crosslinking reaction of a solution under bubbles-containing conditions wherein the solution contains a water-soluble polymer and a crosslinking agent. The present invention further provides this production process. In this production process, the resulting water-swellaable crosslinked polymer having a low bulk density exhibits an absorption capacity of preferably at least 3 g/g, more preferably at least 5 g/g, for physiological saline solution without load. In addition, the water-swellaable crosslinked polymer obtained by this production process is usable as the cationic crosslinked polymer and/or the anionic crosslinked polymer in the water-swellaable crosslinked polymer composition according to the present invention, but is also usable alone.

[0026] When the water-swellaable crosslinked polymer composition according to the present invention is produced using the cationic crosslinked polymer and the anionic crosslinked polymer, a water-swellaable crosslinked polymer composition having high physical properties is obtainable by carrying out a crosslinking reaction in the above way with a polyamine used as the cationic polymer (water-soluble polymer). Thus, the present invention further provides a production process for a water-swellaable crosslinked polymer composition which comprises the steps of: carrying out a crosslinking reaction of a solution under bubbles-containing conditions to obtain a cationic crosslinked polymer wherein the solution contains at least a polyamine and a crosslinking agent; and then mixing the resultant cationic crosslinked polymer and an anionic crosslinked polymer together.

[0027] In addition, if a polyethyleneimine polymer which does not solidify even in a state of high solid content is used, then a cationic crosslinked polymer having so low a bulk density as not to need the drying step can also be obtained directly.

[0028] Incidentally, water-swellaable crosslinked polymer particles of the irregular pulverized shape, which are obtained by drying and then pulverizing a hydrogel resultant from conventional aqueous solution polymerization, usually have a bulk density of more than 0.5 g/ml.

[0029] In addition, the present inventors are the first finders of the cationic crosslinked polymer which has a bulk density of not more than 0.5 g/ml and is water-swellaable and can absorb several times as large a quantity of physiological saline solution as its own weight. The present invention further provides such a cationic crosslinked polymer having a bulk density of not more than 0.5 g/ml and exhibiting an absorption capacity of at least 5 g/g for physiological saline solution without load.

[0030] In the present invention, as to the respective particle diameters of the cationic crosslinked polymer and the anionic crosslinked polymer, not less than 90 weight% of each polymer has a particle diameter in the range of preferably 850 to 100  $\mu$ m, more preferably 500 to 150  $\mu$ m.

[0031] In addition, the weight ratio of the cationic crosslinked polymer to the anionic crosslinked polymer in the present invention is in the range of preferably 10/90 to 80/20, more preferably 20/80 to 80/20, still more preferably 30/70 to 70/30, particularly preferably 40/60 to 60/40, in view of enablement to display the most desalination effect and to display high absorbency for electrolyte solutions.

[0032] The water-swellaable crosslinked polymer composition having a bulk density of not more than 0.5 g/ml, which satisfies requirement (2) above, is easily obtainable by arranging for at least either one of the cationic crosslinked polymer and the anionic crosslinked polymer to have a bulk density of not more than 0.5 g/ml in accordance with requirement (1) above, and it is enough to arrange that the bulk density will not be more than 0.5 g/ml over the whole

composition in consideration of the respective bulk densities of the anionic crosslinked polymer and the cationic crosslinked polymer and the weight ratio between these polymers.

[0033] In addition, the water-swella ble crosslinked polymer composition having a bulk density of not more than 0.5 g/ml, which satisfies requirement (2) above, is producible also by a process including the step of mixing finely-pulverized particles of the cationic crosslinked polymer and finely-pulverized particles of the anionic crosslinked polymer together, for example, in the presence of a binder of which the amount is in the range of 1 to 30 wt%, thereby aggregating and granulating them while forming a polyion complex on their surfaces. However, conventional mixing granulation processes result in a high bulk density, and it is therefore difficult for such conventional mixing granulation process to give the water-swella ble crosslinked polymer according to the present invention.

[0034] The water-swella ble crosslinked polymer composition, according to the present invention, is obtainable by a process including the step of mixing together the cationic crosslinked polymer and the anionic crosslinked polymer, and further, if necessary, another additive. Examples of methods for mixing the cationic crosslinked polymer and the anionic crosslinked polymer together include: a so-called dry-blending method in which both polymers are mixed together in a state where both are dried products; and a so-called gel-blending method in which either one of the polymers is formed into a dry powder, and this dry powder and a (pulverized) gel of the other polymer are mixed together and then pulverized, or in which both polymers are mixed together, in a state where both are gels, and then dried. However, the gel-blending method increases the degree of close contact between particles to result in a high bulk density, therefore the dry-blending method is preferable. Examples of mixers therefor include kneaders, almighty mixers, extruders, Nauta mixers, ribbon mixers, paddle mixers, air mixers, and conical blenders. Incidentally, the "dried product", as referred to in the present invention, is defined as what is in a state where its water content is less than 20 weight% (its solid content is more than 80 weight%). On the other hand, the "gel" is defined as what is in a state where its water content is not less than 20 weight% (its solid content is not more than 80 weight%).

[0035] The water-swella ble crosslinked polymer composition, according to the present invention, may further comprise an additive (e.g. dispersant including inorganic fine particles such as silica) other than the cationic crosslinked polymer and the anionic crosslinked polymer, but needs to be particulate. The total amount of the cationic crosslinked polymer and the anionic crosslinked polymer in the water-swella ble crosslinked polymer composition is preferably not smaller than 95 weight%, more preferably not smaller than 99 weight%.

[0036] The absorption capacity of the water-swella ble crosslinked polymer composition according to the present invention under load is as follows: that in 4 hours is preferably not less than 20 g/g, more preferably not less than 30 g/g, most preferably not less than 40 g/g, and further, that in 20 hours is preferably not less than 30 g/g, more preferably not less than 40 g/g, most preferably not less than 45 g/g.

[0037] The absorption efficiency of the water-swella ble crosslinked polymer composition according to the present invention under load is preferably not less than 1.0, more preferably not less than 1.2, most preferably not less than 1.5.

[0038] The absorption capacity of the water-swella ble crosslinked polymer composition according to the present invention under load is as follows: each of a composition having particle diameters in the range of 850 to 500  $\mu\text{m}$ , a composition having particle diameters in the range of 500 to 300  $\mu\text{m}$ , and a composition having particle diameters of not larger than 300  $\mu\text{m}$  exhibits an absorption capacity under load of preferably not less than 10 g/g in 0.083 hours or not less than 40 g/g in 20 hours.

[0039] The desalting amount of the water-swella ble crosslinked polymer composition according to the present invention is preferably not less than 0.3 g/g, more preferably not less than 0.35 g/g, most preferably not less than 0.4 g/g.

[0040] The water-swella ble crosslinked polymer composition, according to the present invention, can absorb various liquids such as water, body fluids, physiological saline solution, urine, blood, cement water, and fertilizer-containing water, and is therefore usable for absorbent articles which contain this composition. Such absorbent articles are useful for various industrial purposes which need water-absorption, water-holding, wetting, swelling, and gelation, for example, as follows: articles contacting human bodies, such as disposable diapers, sanitary napkins, and incontinent pads; materials to separate water from oil; other dehydrating or drying agents; water-holding materials for plants or soil; solidifiers for muddy sediment; dewfall preventives; sealing materials for electric wires or optical fibers; and sealing materials for engineering works or constructions.

[0041] The structure of the above absorbent articles is, for example, such that an absorbent layer containing the water-swella ble crosslinked polymer composition according to the present invention is interposed between a sheet with liquid permeability and a sheet with liquid impermeability.

[0042] The above-mentioned sheet with liquid permeability is a sheet comprising a material that is permeable with aqueous liquids. Examples thereof include: nonwoven fabrics, woven fabrics; porous synthetic resins in films of polyethylene, polypropylene, polyester, polyamide. In addition, the above-mentioned sheet with liquid impermeability is a sheet comprising a material that is impermeable with aqueous liquids. Examples thereof include: synthetic resins in films of polyethylene, polypropylene, ethylene vinyl acetate, polyvinyl chloride, films of combined materials of these synthetic resins with nonwoven fabrics; films of combined materials of the above-mentioned synthetic resins with woven fabrics.

Incidentally, the sheet with liquid impermeability may be permeable with vapor.

[0043] In addition, when the water-swellaible crosslinked polymer composition according to the present invention is used for the absorbent article, a product by beforehand mixing the cationic crosslinked polymer and the anionic crosslinked polymer together in the aforementioned way may be used as the water-swellaible crosslinked polymer composition, but it is also permissible to use the water-swellaible crosslinked polymer composition according to the present invention in a form such that the cationic crosslinked polymer and the anionic crosslinked polymer will be mixed together when the absorbent article is produced.

[0044] Incidentally, it is permissible to give various functions to the water-swellaible crosslinked polymer composition according to the present invention on the absorbent article by further adding materials, such as deodorants, antimicrobial agents, perfumes, various inorganic powders, foaming agents, pigments, dyes, hydrophilic short fibers, manure, oxidants, reductants, water, and salts, to the water-swellaible crosslinked polymer composition according to the present invention.

(Effects and Advantages of the Invention):

[0045] Because the water-swellaible crosslinked polymer composition according to the present invention comprises a combination of the anionic water-swellaible crosslinked polymer particle with the cationic water-swellaible crosslinked polymer particle, an neutralized structure is formed from an acid group of the former polymer particle and a basic group of the latter polymer particle in the above composition, with the result that each of these polymer particles becomes so water-swellaible that the above composition can exhibit more excellent swellability than conventional neutralized water-absorbent resins, and further can also take electrolytes (which are problems to the conventional neutralized water-absorbent resins) in to prevent the salt effect and, as a result, can enhance the ability to absorb the electrolyte solutions much more than conventional cases. Furthermore, the above composition is a water-swellaible crosslinked polymer composition which is excellent in the absorption properties under load and is therefore highly practicable.

[0046] The water-swellaible crosslinked polymer according to the present invention easily gives the above water-swellaible crosslinked polymer composition according to the present invention. And the production process for a water-swellaible crosslinked polymer, according to the present invention, easily gives the above water-swellaible crosslinked polymer according to the present invention.

[0047] The production process for a water-swellaible crosslinked polymer composition, according to the present invention, easily gives the above water-swellaible crosslinked polymer composition according to the present invention.

[0048] Because the absorbent article according to the present invention includes the above water-swellaible crosslinked polymer composition according to the present invention as a component, this absorbent article is an article which is excellent in the absorption properties under load and is therefore highly practicable.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0049] Hereinafter, the present invention is more specifically illustrated by the following examples of some preferred embodiments in comparison with comparative examples not according to the invention. However, the present invention is not limited thereto.

[0050] In the examples, unless otherwise noted, the units "part(s)" and "%" denote those by weight.

[0051] Incidentally, the physical properties of the water-swellaible crosslinked polymer composition were measured in the following ways.

(a) Absorption capacity for physiological saline solution without load:

[0052] First, 0.2 g of crosslinked polymer particles were uniformly placed into a nonwoven fabric-made bag (60 mm x 80 mm) and then immersed into a 0.9 weight % aqueous sodium chloride solution (physiological saline solution). Sixty minutes later, the bag was drained up and then drained at 250 G for 3 minutes with a centrifuge, and the weight W1 (g) of the bag was then measured. On the other hand, the same procedure was carried out without the crosslinked polymer particles, and the resultant weight W0 (g) was measured. Thus, the absorption capacity (g/g) without load was calculated in accordance with the following equation:

$$\text{Absorption capacity (g/g) without load} = (W1(g) - W0(g)) / (\text{weight (g) of crosslinked polymer particles} - 1)$$

[0053] Incidentally, when the absorption capacity without load in the present invention was measured, particles having particle diameters in the range of 500 to 300  $\mu\text{m}$  were used.



(b) Absorption capacity under load:

[0054] First, 0.9 g of water-swellaible crosslinked polymer composition was uniformly spread on a stainless wire gauze of 400 mesh (mesh opening size: 38  $\mu\text{m}$ ) as attached by fusion to the bottom of a plastics supporting cylinder with an inner diameter of 60 mm. Next, a piston and a load were mounted in sequence on the above water-swellaible crosslinked polymer composition, wherein the piston had an outer diameter of only a little smaller than 60 mm and made of gap with the wall face of the supporting cylinder, but was not hindered from moving up and down, and wherein the total weight of the piston and the load were adjusted such that a load of 50g/cm<sup>2</sup> could uniformly be applied to the water-swellaible crosslinked polymer composition. Then, the weight (W<sub>a</sub>) of the resultant set of measurement apparatus was measured.

[0055] A glass filter plate of 90 mm in diameter was mounted inside a Petri dish of 150 mm in diameter, and as salt water (1,000 g) of total weight as prepared by adding deionized water (solvent) to 2.0 g of potassium chloride, 2.0 g of sodium sulfate, 0.85 g of ammonium dihydrogen phosphate, 0.15 g of diammonium hydrogen phosphate, 0.25 g of calcium chloride dihydrate, and 0.5 g of magnesium chloride hexahydrate) was added up to the same level as the surface of the glass filter plate, on which filter paper of 90 mm in diameter was then mounted such that its entire surface would be wetted, and further, an excess of liquid was removed.

[0056] The above set of measurement apparatus was mounted on the above wet filter paper, thereby allowing the water-swellaible crosslinked polymer composition to absorb the liquid under load. After the water-swellaible crosslinked polymer composition had absorbed the liquid for a predetermined time, the set of measurement apparatus was lifted to measure its weight (W<sub>b</sub>) again. Then, the absorption capacity under load was determined from the below-mentioned equation. The above measurement was carried out with the piston and the load still mounted. After the measurement of the weight had ended, the set of measurement apparatus was mounted on the above wet filter paper again, thereby allowing the water-swellaible crosslinked polymer composition to absorb the salt water under load until the next predetermined time. Thereafter, the above operation was repeated to compare the salt water absorption rate. The larger the salt water absorption capacity as exhibited per unit time is, the faster the salt water absorption rate is.

$$\text{Absorption capacity (g/g) under load} \\ = (W_b(g) - W_a(g)) / (\text{weight (g) of water-swellaible crosslinked polymer composition})$$

(c) Absorption efficiency under load and absorption capacity of upper, intermediate, and lower layers of gel under load:

[0057] The absorption efficiency under load was determined by a method as described in JP-A-265582/1998 as follows. Immediately after the above measurement of the absorption capacity under load had been carried out for 4 hours, the set of measurement apparatus was removed from the filter paper in a state where the water-swellaible crosslinked polymer composition which had absorbed the salt water and swollen therewith (i.e. swollen gel) was present in the supporting cylinder and still carried the piston and the load. Then, the set of measurement apparatus was mounted on a stack of 10 pieces of filter paper of 90 mm in diameter (No. 2, produced by Advantech Toyo K.K.) for 2 minutes to remove the salt water which was present in the supporting cylinder and between swollen gel particles (gaps salt water which had not been absorbed by the water-swellaible crosslinked polymer composition). Then, weight W<sub>c</sub>(g) was measured in a state where the swollen gel was present in the supporting cylinder and still carried the piston and the load. Weight W<sub>d</sub>(g) of the supporting cylinder, which had been measured beforehand, and the total weight W<sub>e</sub>(g) of the piston and the load were subtracted from W<sub>c</sub>(g) to determine weight W<sub>f</sub>(g) of the swollen gel from which the gaps salt water had been removed.

[0058] Next, the piston and the load were removed from the supporting cylinder, and then the swollen gel in the supporting cylinder was got out every one-third of the weight W<sub>f</sub>(g) of the swollen gel from the top to obtain upper, intermediate, and lower layers of the gel. The resultant upper layer of the gel was weighed out onto an aluminum cup and then dried at 180 °C for 3 hours, and then the weight of the resultant dried product was corrected by the solid content of the absorbed salt water to determine absorption capacity G1 (g/g) of the upper layer of the gel under load, when the absorption capacity of the gel under load was calculated on the assumption that 50 % of the components of the salt water were taken into the water-swellaible crosslinked polymer composition (on the assumption that the concentration of the salt water taken into the water-swellaible crosslinked polymer composition was 50 % of the concentration of the original salt water).

[0059] The same procedure as the above was carried out also for the lower and intermediate layers of the gel to determine absorption capacity G2 (g/g) of the lower layer of the gel under load and an absorption capacity of the intermediate layer of the gel under load.

[0060] Then, the absorption efficiency under load was calculated in accordance with the following equation:

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Absorption efficiency under load =  $G1/G2$

(d) Bulk density:

[0061] The bulk density was determined by a method as described in the Japanese Industrial Standard (JIS) K3362 8.2. Incidentally, as to the measurement device, a bulk density meter (produced by Kuramochi Scientific Instrument Seisakusho K.K.) was used.

[0062] An amount of 120 ml of sample, which had been well-mixed to eliminate the unevenness according to the particle diameter distribution, was placed into a funnel with its damper closed. Immediately thereafter, the damper was opened to drop the sample into a receiver. A portion, as overbrimmed from the receiver, of the sample was scraped off with a glass rod. Then, the weight of the receiver containing the sample was measured with an accuracy to 0.1 g to calculate the bulk density in accordance with the below-mentioned equation. Incidentally, the bulk density was measured under conditions where the solid content (based on the moisture content) of the crosslinked polymer particles or water-swella-

$\pm 2^{\circ}\text{C}$ ,

$$\text{Bulk density (g/ml)} = (C - A) / B$$

where

A: weight (g) of the receiver

B: capacity of the receiver (ml)

C: weight (g) of the receiver when containing the sample

(e) Solid content:

[0063] The weight of an aluminum dish of 50 mm in diameter was measured with an accuracy to 0.0001 g (the resultant weight was referred to as  $W_a$ ). About 1 g of sample was weighed out with an accuracy to 0.0001 g (the resultant weight was referred to as  $W_b$ ), and then uniformly spread out on the above aluminum dish, and then dried at  $150^{\circ}\text{C}$  with a wind-free drying oven. After 1 hour, the sample was got out of the drying oven, and then left cooling in a desiccator for about 10 minutes, and then weighed with an accuracy to 0.0001 g (the resultant weight was referred to as  $W_c$ ). The solid content was calculated in accordance with the following equation:

$$\text{Solid content (wt\%)} = (W_c - W_a) / W_b$$

(f) Desalting amount:

[0064] First, 1.0 g of water-swella-

$$\text{Desalting amount (g/g)} = 0.9 - W1 \times C1 / 100$$

(EXAMPLE-1):

[0065] First, 1,000 g of 30% polyethylenimine (trade name: Epomin P-1000, produced by Nippon Shokubai Co., Ltd.) was placed into a beaker of 2 liters as furnished with stirrer to stir the contents. Next, 30 g of ethyleneglycoldiglycidyl ether (trade name: Denacol EX-810, produced by Nagase Chemicals, Ltd.) (crosslinking agent) was added thereto under stirring. Then, the resultant mixture was stirred for 1 minute to obtain a homogeneous solution. Thereafter, the vessel was sealed, and then placed into an incubator of  $60^{\circ}\text{C}$  to carry out a reaction. After 3 hours, the system temperature was cooled down to room temperature, and the resultant lumped gel was pulverized with a laboratory pulverizer into particles of diameters of not larger than  $850\text{ }\mu\text{m}$ . The resultant powdery hydrogel was dried at  $60^{\circ}\text{C}$  with hot air for 2 hours, and then 0.9 g of inorganic fine particles (trade name: Aerosil R972, produced by Nippon Aerosil Co., Ltd.) were added to the resultant dried product, and they were well blended so that the inorganic fine particles could uniformly be dispersed. The resultant blend was pulverized with a laboratory pulverizer into particle diameters of not

larger than 850  $\mu\text{m}$ , thus obtaining cationic crosslinked polymer particles (A1). The 850- $\mu\text{m}$ -passed yield was 96.5%. The crosslinked polymer particles (A1) exhibited an absorption capacity of 6.5g/g for physiological saline solution without load. In addition, the crosslinked polymer particles (A1) comprised: particles of 850 to 500  $\mu\text{m}$  in the ratio of 29.3%; particles of 500 to 300  $\mu\text{m}$  in the ratio of 39.4%; particles of 300 to 150  $\mu\text{m}$  in the ratio of 27.6%; and particles of not larger than 150  $\mu\text{m}$  in the ratio of 3.7%. In addition, the solid content and the bulk density of the crosslinked polymer particles (A1) were measured, and the results are shown in Table 1.

## (EXAMPLEA-2):

- 10 [0066] First, 1,000g of 30% polyethylenimine (tradename: Epomin P-1000, produced by Nippon Shokubai Co., Ltd.) was placed into a beaker of 2 liters as furnished with stirrer to stir the contents. Next, a crosslinking agent solution was added thereto under stirring, where the crosslinking agent solution was prepared by dissolving 18g of N,N'-methylenebisacrylamide (produced by Nitto Chemical Industry Co., Ltd.) (crosslinking agent) into a mixed solvent of 100g of pure water and 200g of methanol. Then, the resultant mixture was stirred for 1 minute to obtain a homogeneous solution. Thereafter, the vessel was sealed, and then placed into an incubator of 60  $^{\circ}\text{C}$  to carry out a reaction. After 3 hours, the system temperature was cooled down to room temperature, and the resultant lumped gel was pulverized with a meat chopper with 2.4 mm aperture. The resultant powdery hydrogel was dried at 60  $^{\circ}\text{C}$  with hot air for 2 hours, and then 3g of inorganic fine particles (tradename: Aerosil R972, produced by Nippon Aerosil Co., Ltd.) were added to the resultant dried product, and they were well blended so that the inorganic fine particles could uniformly be dispersed. The resultant blend was pulverized with a laboratory pulverizer into particle diameters of not larger than 850  $\mu\text{m}$ , thus obtaining cationic crosslinked polymer particles (A2). The 850- $\mu\text{m}$ -passed yield was 76.1%. The crosslinked polymer particles (A2) exhibited an absorption capacity of 9.2g/g for physiological saline solution without load. In addition, the crosslinked polymer particles (A2) comprised: particles of 850 to 500  $\mu\text{m}$  in the ratio of 54.3%; particles of 500 to 300  $\mu\text{m}$  in the ratio of 33.8%; particles of 300 to 150  $\mu\text{m}$  in the ratio of 11.3%; and particles of not larger than 150  $\mu\text{m}$  in the ratio of 0.6%. In addition, the solid content and the bulk density of the crosslinked polymer particles (A2) were measured, and the results are shown in Table 1.

## (EXAMPLEA-3):

- 30 [0067] First, 1,000g of 30% polyethylenimine (tradename: Epomin P-1000, produced by Nippon Shokubai Co., Ltd.) was placed into a beaker of 2 liters as furnished with stirrer to stir the contents. Next, a crosslinking agent solution was added thereto under stirring, where the crosslinking agent solution was prepared by dissolving 30g of N,N'-methylenebisacrylamide (produced by Nitto Chemical Industry Co., Ltd.) (crosslinking agent) into a mixed solvent of 200g of pure water and 200g of methanol. Then, the resultant mixture was stirred for 1 minute to obtain a homogeneous solution. Thereafter, the vessel was sealed, and then placed into an incubator of 60  $^{\circ}\text{C}$  to carry out a reaction. After 3 hours, the system temperature was cooled down to room temperature, and the resultant lumped gel was pulverized with a laboratory pulverizer into particle diameters of not larger than 850  $\mu\text{m}$ . The resultant powdery hydrogel was dried at 60  $^{\circ}\text{C}$  with hot air for 2 hours, and then 0.9g of inorganic fine particles (tradename: Aerosil R972, produced by Nippon Aerosil Co., Ltd.) were added to the resultant dried product, and they were well blended so that the inorganic fine particles could uniformly be dispersed. The resultant blend was pulverized with a laboratory pulverizer into particle diameters of not larger than 850  $\mu\text{m}$ , thus obtaining cationic crosslinked polymer particles (A3). The 850- $\mu\text{m}$ -passed yield was 98%. An electron photomicrograph of the crosslinked polymer particles (A3) is shown in Fig. 1. The crosslinked polymer particles (A3) exhibited an absorption capacity of 7.6g/g for physiological saline solution without load. In addition, the crosslinked polymer particles (A3) comprised: particles of 850 to 500  $\mu\text{m}$  in the ratio of 22.6%; particles of 500 to 300  $\mu\text{m}$  in the ratio of 35.1%; particles of 300 to 150  $\mu\text{m}$  in the ratio of 34.6%; and particles of not larger than 150  $\mu\text{m}$  in the ratio of 7.7%. In addition, the solid content and the bulk density of the crosslinked polymer particles (A3) were measured, and the results are shown in Table 1.

## (COMPARATIVEEXAMPLEA-1):

- 50 [0068] First, 600ml of cyclohexane solution, containing 6g of inorganic fine particles (tradename: Aerosil R972, produced by Nippon Aerosil Co., Ltd.), was placed into a separable flask of 2 liters with a dropping funnel, a stirrer, a thermometer, a reflux condenser, and a built-in baffle, and then stirred at room temperature. Next, a crosslinking agent solution, as prepared by dissolving 10.12g of N,N'-methylenebisacrylamide (produced by Nitto Chemical Industry Co., Ltd.) (as the crosslinking agent) into a mixed solvent comprising 50g of pure water and 100g of methanol, was added under stirring to an aqueous hydrophilic high-molecular compound solution having been cooled to 60  $^{\circ}\text{C}$ . Beforehand and comprising 337.3g of 30% polyethylenimine (tradename: Epomin P-1000, produced by Nippon Shokubai Co., Ltd.) and 102.5g of pure water, thus preparing an aqueous liquid containing a crosslinking agent and a hydrophilic high-molec-

ular compound. Then, this solution was added to the above cyclohexanes solution at room temperature under stirring. Under stirring, the temperature of the system was gradually raised to 65 °C, and the reaction was carried out at 65 °C for 3 hours. Then, the temperature of the system was cooled to room temperature, and the resultant spherical hydrogel was filtrated by suction, and then not washed with water, but dried at 60 °C with hot air for 2 hours, thus obtaining cationic crosslinked polymer particles (A4). This crosslinked polymer particles (A4) exhibited an absorption capacity of 7.0 g/g for physiological saline solution without load. In addition, the crosslinked polymer particles (A4) comprised: particles of 850 to 500 μm in theratio of 54.1%; particles of 500 to 300 μm in theratio of 29.9%; particles of 300 to 150 μm in theratio of 14.2%; and particles of not larger than 150 μm in theratio of 1.8%. In addition, the solid content and the bulk density of the crosslinked polymer particles (A4) were measured, and their results are shown in Table 1.

#### (COMPARATIVE EXAMPLE A-2):

[0069] First, 600 ml of cyclohexanes solution, containing 6 g of inorganic fine particles (trade name: Aerosil R972, produced by Nippon Aerosil Co., Ltd.), was placed into a separable flask of 2 liters with dropping funnel, stirrer, a thermometer, a reflux condenser, and a built-in baffle, and then stirred at room temperature. Next, 21.8 g of 50% aqueous solution of polyethylene glycol diglycidyl ether (trade name: Denacol EX-810, produced by Nagase Chemicals, Ltd.) (as the crosslinking agent) was added under stirring to an aqueous hydrophilic high-molecular compound solution having been cooled to 0 °C before hand and comprising 337.3 g of 30% polyethyleneimine (trade name: Epomin P1000, produced by Nippon Shokubai Co., Ltd.) and 102.5 g of pure water, thus preparing an aqueous liquid containing a crosslinking agent and a hydrophilic high-molecular compound. Then, this solution was added to the above cyclohexanes solution at room temperature under stirring. Under stirring, the temperature of the system was gradually raised to 65 °C, and the reaction was carried out at 65 °C for 3 hours. Then, the temperature of the system was cooled to room temperature, and the resultant spherical hydrogel was filtrated by suction, and then not washed with water, but dried at 60 °C with hot air for 2 hours, thus obtaining cationic crosslinked polymer particles (A5). An electron photomicrograph of the crosslinked polymer particles (A5) is shown in Fig. 2. This crosslinked polymer particles (A5) exhibited an absorption capacity of 9.5 g/g for physiological saline solution without load. In addition, as to the crosslinked polymer particles (A5), they had particles of 850 to 150 μm was 99% of the charged draw materials. In addition, the crosslinked polymer particles (A5) comprised: particles of 850 to 500 μm in theratio of 1.9%; particles of 500 to 300 μm in theratio of 43.0%; particles of 300 to 150 μm in theratio of 44.1%; and particles of not larger than 150 μm in theratio of 1.0%. The solid content and the bulk density of the crosslinked polymer particles (A5) were measured, and their results are shown in Table 1.

#### (REFERENTIAL EXAMPLE B-1)

[0070] First, 70.00 parts of acrylic acid, 0.15 parts of N,N'-methylenebisacrylamide (copolymerizable crosslinking agent), and 275.32 parts of deionized water were mixed. The resultant mixture was degassed with nitrogen gas for 60 minutes and then put into an airtight vessel possible to open and close, and the displacement of the internal air of the reaction system with nitrogen was continued with the liquid temperature kept at 23 °C under the nitrogen atmosphere. Next, 2.12 parts of 10 weight % aqueous 2,2'-azobis(2-amidinopropane) dihydrochlorides solution, 0.67 part of 10 weight % aqueous hydrogen peroxides solution, and 1.75 parts of 1 weight % aqueous L-ascorbic acid solution were added under stirring. As a result, after 3 minutes, apolymerization reaction got started, and after 25 minutes, the reaction system reached the peak temperature. Thirty minutes after the polymerization temperature reached its peak, the resultant crosslinked hydrogel polymer was got out and then caused to pass through a meat chopper, thus obtaining a crosslinked hydrogel polymer as finely divided. This polymer was dried in a hot-air drier at 60 °C for 1 hour. The resultant dried product was pulverized with a laboratory pulverizer, and the resultant pulverized product was sieved with a wire gauze of 850 μm in mesh opening size to separate what passed through it, thus obtaining anionic crosslinked polymer particles (B1). This crosslinked polymer particles (B1) exhibited an absorption capacity of 7.1 g/g for physiological saline solution without load. The crosslinked polymer particles (B1) comprised: particles of 850 to 500 μm in theratio of 33.7%; particles of 500 to 300 μm in theratio of 45.3%; particles of 300 to 150 μm in theratio of 19.8%; and particles of not larger than 150 μm in theratio of 1.2%.

#### (REFERENTIAL EXAMPLE B-2)

[0071] First, 70.00 parts of acrylic acid, 0.30 parts of N,N'-methylenebisacrylamide (copolymerizable crosslinking agent), and 275.17 parts of deionized water were mixed. The resultant mixture was degassed with nitrogen gas for 60 minutes and then put into an airtight vessel possible to open and close, and the displacement of the internal air of the reaction system with nitrogen was continued with the liquid temperature kept at 23 °C under the nitrogen atmosphere. Next, 2.12 parts of 10 weight % aqueous 2,2'-azobis(2-amidinopropane) dihydrochlorides solution, 0.67 part of 10 weight

%aqueous hydrogen peroxide solution, and 1.75 parts of 1 weight % aqueous L-ascorbic acid solution were added under stirring. As a result, after 3 minutes, a polymerization reaction got started, and after 25 minutes, the reaction system reached the peak temperature. Thirty minutes after the polymerization temperature reached its peak, the resultant crosslinked hydrogel polymer was got out and then caused to pass through a meat chopper, thus obtaining a crosslinked hydrogel polymer as finely divided. This polymer was dried in a hot-air drier for 150 °C for 1 hour. The resultant dried product was pulverized with a laboratory pulverizer, and the resultant pulverized product was sieved with a wire gauze of 850 μm in mesh opening size to separate what passed through it, thus obtaining an anionic crosslinked polymer particles (B2). This crosslinked polymer particles (B2) exhibited an absorption capacity of 5.9g/g for physiological saline solution without load. The crosslinked polymer particles (B2) comprised: particles of 850 to 500 μm in ratio of 39.0%; particles of 500 to 300 μm in ratio of 39.0%; particles of 300 to 150 μm in ratio of 21.8%; and particles of not larger than 150 μm in ratio of 0.2%.

## (REFERENTIAL EXAMPLE B-3)

**[0072]** First, 70.00 parts of acrylic acid, 0.45 parts of N,N'-methylenebisacrylamide (copolymerizable crosslinking agent), and 274.99 parts of deionized water were mixed. The resultant mixture was degassed with nitrogen gas for 60 minutes and then put into an airtight vessel possible to open and close, and the displacement of the internal air of the reaction system with nitrogen was continued with the liquid temperature kept at 23 °C under the nitrogen atmosphere. Next, 2.12 parts of 10 weight % aqueous 2,2'-azobis(2-amidinopropane) dihydrochloride solution, 0.7 part of 10 weight % aqueous hydrogen peroxide solution, and 1.75 parts of 1 weight % aqueous L-ascorbic acid solution were added under stirring. As a result, after 3 minutes, a polymerization reaction got started, and after 25 minutes, the reaction system reached the peak temperature. Thirty minutes after the polymerization temperature reached its peak, the resultant crosslinked hydrogel polymer was got out and then caused to pass through a meat chopper, thus obtaining a crosslinked hydrogel polymer as finely divided. This polymer was dried in a hot-air drier for 150 °C for 1 hour. The resultant dried product was pulverized with a laboratory pulverizer, and the resultant pulverized product was sieved with a wire gauze of 850 μm in mesh opening size to separate what passed through it, thus obtaining an anionic crosslinked polymer particles (B3). This crosslinked polymer particles (B3) exhibited an absorption capacity of 5.6g/g for physiological saline solution without load. The crosslinked polymer particles (B3) comprised: particles of 850 to 500 μm in ratio of 34.1%; particles of 500 to 300 μm in ratio of 42.5%; particles of 300 to 150 μm in ratio of 22.1%; and particles of not larger than 150 μm in ratio of 1.3%. In addition, the solid content and the bulk density were measured, and the results are shown in Table 1.

## (REFERENTIAL EXAMPLE B-4)

**[0073]** First, 70.00 parts of acrylic acid, 0.60 parts of N,N'-methylenebisacrylamide (copolymerizable crosslinking agent), and 274.84 parts of deionized water were mixed. The resultant mixture was degassed with nitrogen gas for 60 minutes and then put into an airtight vessel possible to open and close, and the displacement of the internal air of the reaction system with nitrogen was continued with the liquid temperature kept at 23 °C under the nitrogen atmosphere. Next, 2.12 parts of 10 weight % aqueous 2,2'-azobis(2-amidinopropane) dihydrochloride solution, 0.7 part of 10 weight % aqueous hydrogen peroxide solution, and 1.75 parts of 1 weight % aqueous L-ascorbic acid solution were added under stirring. As a result, after 3 minutes, a polymerization reaction got started, and after 25 minutes, the reaction system reached the peak temperature. Thirty minutes after the polymerization temperature reached its peak, the resultant crosslinked hydrogel polymer was got out and then caused to pass through a meat chopper, thus obtaining a crosslinked hydrogel polymer as finely divided. This polymer was dried in a hot-air drier for 150 °C for 1 hour. The resultant dried product was pulverized with a laboratory pulverizer, and the resultant pulverized product was sieved with a wire gauze of 850 μm in mesh opening size to separate what passed through it, thus obtaining an anionic crosslinked polymer particles (B4). This crosslinked polymer particles (B4) exhibited an absorption capacity of 5.2g/g for physiological saline solution without load. The crosslinked polymer particles (B4) comprised: particles of 850 to 500 μm in ratio of 36.3%; particles of 500 to 300 μm in ratio of 42.5%; particles of 300 to 150 μm in ratio of 20.3%; and particles of not larger than 150 μm in ratio of 0.9%.

Table1

	Crosslinkedpolymer particles	Particlediameter( $\mu$ m)	Solidcontent(%)	Bulkdensity(g/ml)
5	ExampleA-1	850to500	88.6	0.393
		500to300	87.4	0.353
		300to150	86.6	0.314
10		Whole(notlargerthan850)	87.3	0.310
	ExampleA-2	850to500	85.8	0.237
		500to300	85.9	0.252
15		300to150	85.5	0.260
		Whole(notlargerthan850)	85.7	0.257
	ExampleA-3	850to500	90.9	0.269
20		500to300	90.9	0.281
		300to150	90.9	0.314
		Whole(notlargerthan850)	90.9	0.297
	Comparative ExampleA-1	850to500	87.3	0.610
25		500to300	87.1	0.617
		300to150	85.9	0.634
		Whole(notlargerthan850)	86.3	0.625
	Comparative ExampleA-2	850to500	85.4	0.660
30		500to300	85.3	0.601
		300to150	84.8	0.644
		Whole(notlargerthan850)	85.1	0.654
	ReferentialExampleB-3	850to500	98.4	0.620
35		500to300	98.4	0.616
		300to150	98.1	0.610
40		Whole(notlargerthan850)	98.3	0.625

(EXAMPLES1to4):

[0074] Onehundredweightpartsofparticles, havingparticlediametersintherangeof500to300  $\mu$ m, ofthecationiccrosslinkedpolymerparticles(A3)weredry-blendedwith100weightpartsofanioniccrosslinkedpolymerparticles (B1),(B2),(B3),and(B4)(havingparticlediametersofnotlargerthan850  $\mu$ m)respectively, thusobtaining200weight partsofparticulatewater-swellablecrosslinkedpolymercompositions(1),(2),(3),and(4)respectively. Theirabsorption capacitiesforasaltwater(1,000gintotalweightaspreparedbyaddingdeionizedwater(solvent)to2.0gofpotassium chloride, 2.0gofsodiumsulfate, 0.85gofammonium dihydrogenphosphate, 0.15gofdiammonium hydrogenphosphate, 0.25gofcalciumchloridedihydrate, and0.5gofmagnesiumchloridehexahydrate)underloadin4hoursand in20hoursareshowninTable2. TherresultsareshowninFigs.3and4. Fig.3showstheabsorptioncapacitiesunder loadin4hours, andFig.4showstheabsorptioncapacitiesunderloadin20hours.

(COMPARATIVEEXAMPLES1to4):

[0075] Onehundredweightpartsofparticles, havingparticlediametersintherangeof500to300  $\mu$ m, ofthecationiccrosslinkedpolymerparticles(A4)weredry-blendedwith100weightpartsofanioniccrosslinkedpolymerparticles (B1),(B2),(B3),and(B4)(havingparticlediametersofnotlargerthan850  $\mu$ m)respectively, thusobtaining200weight

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partsofparticulatewater-swella-blecrosslinkedpolymercompositions(5),(6),(7),and(8)respectively.Theirabsorption capacitiesforasaltwater(1,000gintotalweightaspreparedbyaddingdeionizedwater(solvent)to2.0gofpotassium chloride, 2.0gofsodiumsulfate, 0.85gofammoniumdihydrogenphosphate, 0.15gofdiammoniumhydrogenphos-  
 5 phate, 0.25gofcalciumchloridedihydrate, and0.5gofmagnesiumchloridehexahydrate)underloadin4hoursand in20hoursareshowninTable3.TheirresultsareshowninFigs.3and4.Fig.3showstheabsorptioncapacitiesin4 hours,andFig.4showstheabsorptioncapacitiesin20hours.

Table2

	Water-swella-blecrosslinked polymercom- position	Cationic crosslinkedpol- ymerparticles	Anionic crosslinkedpol- ymerparticles	Bulkdensity (g/ml)	Absorptioncapacity(g/g) underload	
					4hours	20hours
Example1	(1)	(A3)	(B1)	0.395	44.1	48.7
Example2	(2)	(A3)	(B2)	0.386	43.3	47.3
Example3	(3)	(A3)	(B3)	0.397	41.7	45.3
Example4	(4)	(A3)	(B4)	0.381	40.4	44.8

Table3

	Water-swella-blecrosslinked polymercom- position	Cationic crosslinked polymerparti- cles	Anionic crosslinked polymerparti- cles	Bulkdensity (g/ml)	Absorptioncapacity(g/g) underload	
					4hours	20hours
Comparative Example1	(5)	(A4)	(B1)	0.612	29.4	33.3
Comparative Example2	(6)	(A4)	(B2)	0.605	37.3	42.6
Comparative Example3	(7)	(A4)	(B3)	0.597	36.7	41.1
Comparative Example4	(8)	(A4)	(B4)	0.610	35.4	40.4

[0076] AsisshowninTables2and3,theabsorptioncapacitiesunderloadin4hoursandin20hoursarehigherin Examples1to4inwhichacationiccrosslinkedpolymerhavingabulkdensityofnotmorethan0.5g/mlwasusedthan inComparativeExamples1to4inwhichacationiccrosslinkedpolymerhavingabulkdensityofmorethan0.5g/mlwas used. Thattheabsorptioncapacityunderloadin4hoursishighmeansthatthesaltwaterabsorptionrateisfast.The absorptioncapacityunderloadin20hoursindicatesalmostthesaturatedvalue,thereforethatthisishighmeansthat thesaturatedabsorptioncapacityvalue(absorptionquantity)underloadishigh.

(EXAMPLES5and6):

[0077] Theparticulatewater-swella-blecrosslinkedpolymercompositions(1)and(3)resultantfromExamples1and 3respectivelyweremeasuredbytheabsorptioncapacitiesoftheupper,intermediate,andlowerlayersofthegelunder loadin4hoursandtheabsorptionefficiencyunderloadin4hours.TheirresultsareshowninTable4.

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(COMPARATIVEEXAMPLES5and6):

**[0078]** The particulate water-swella ble crosslinked polymer compositions (5) and (7) resultant from Comparative Examples 1 and 3 respectively were measured by the absorption capacities of the upper, intermediate, and lower layers of the gel under load in 4 hours and the absorption efficiency under load in 4 hours. Their results are shown in Table 4.

Table 4

	Water-swella ble crosslinked polymer composition	Absorption capacity (g/g) of upper layer of gel	Absorption capacity (g/g) of intermediate layer of gel	Absorption capacity (g/g) of lower layer of gel	Absorption efficiency under load
Example 5	(1)	51.6	49.1	27.4	1.88
Example 6	(3)	48.1	46.3	30.1	1.60
Comparative Example 5	(5)	30.8	28.8	27.6	1.12
Comparative Example 6	(7)	35.4	42.9	33.3	1.06

**[0079]** As is shown in Table 4, the absorption efficiency under load is higher in Examples 5 and 6 in which a cationic crosslinked polymer having a bulk density of not more than 0.5 g/ml was used than in Comparative Examples 5 and 6 in which a cationic crosslinked polymer having a bulk density of more than 0.5 g/ml was used. This indicates that the liquid permeability from the lower layer (which is the closest to the liquid-absorbed portion) to the upper layer (which is the farthest from the liquid-absorbed portion) is high, wherefrom it would be understood that efficient water absorption was made.

(EXAMPLE 7):

**[0080]** Particles having particle diameters in the range of 850 to 500  $\mu\text{m}$ , particles having particle diameters in the range of 500 to 300  $\mu\text{m}$ , and particles having particle diameters of not larger than 300  $\mu\text{m}$ , of the cationic crosslinked polymer particles (A3), were dry-blended in a amount of 100 weight parts respectively with 100 weight parts of anionic crosslinked polymer particles (B3) (having particle diameters of not larger than 850  $\mu\text{m}$ ), thus obtaining 200 weight parts of particulate water-swella ble crosslinked polymer compositions (9) to (11) respectively. Their absorption capacities for a salt water (1,000 g in total weight) as prepared by adding deionized water (solvent) to 2.0 g of potassium chloride, 2.0 g of sodium sulfate, 0.85 g of ammonium dihydrogen phosphate, 0.15 g of diammonium hydrogen phosphate, 0.25 g of calcium chloride dihydrate, and 0.5 g of magnesium chloride hexahydrate) under load (in 0.083 hour, in 0.5 hour, in 1 hour, in 4 hours, and in 20 hours) are shown in Table 5.

(COMPARATIVEEXAMPLE 7):

**[0081]** Particles having particle diameters in the range of 850 to 500  $\mu\text{m}$ , particles having particle diameters in the range of 500 to 300  $\mu\text{m}$ , and particles having particle diameters of not larger than 300  $\mu\text{m}$ , of the cationic crosslinked polymer particles (A4), were dry-blended in a amount of 100 weight parts respectively with 100 weight parts of anionic crosslinked polymer particles (B3) (having particle diameters of not larger than 850  $\mu\text{m}$ ), thus obtaining 200 weight parts of particulate water-swella ble crosslinked polymer compositions (12) to (14) respectively. Their absorption capacities for a salt water (1,000 g in total weight) as prepared by adding deionized water (solvent) to 2.0 g of potassium chloride, 2.0 g of sodium sulfate, 0.85 g of ammonium dihydrogen phosphate, 0.15 g of diammonium hydrogen phosphate, 0.25 g of calcium chloride dihydrate, and 0.5 g of magnesium chloride hexahydrate) under load (in 0.083 hour, in 0.5 hour, in 1 hour, in 4 hours, and in 20 hours) are shown in Table 5.



Table5

5			ComparativeExample7			Example7		
	Particlediameter( $\mu$ m)		850to500	500to300	Notlarger than300	850to500	500to300	Notlarger than300
	Water-swella-blecrosslinked polymercomposition		(9)	(10)	(11)	(12)	(13)	(14)
10	Absorption capacity (g/g)under load	0.083hr	7.3	9.4	11.8	12.0	15.1	15.9
		0.5hr	15.8	20.5	21.8	23.7	27.8	28.6
		1hr	21.0	26.6	26.0	28.5	33.3	33.5
15		4hr	31.4	36.7	36.9	36.6	41.7	40.5
		20hr	38.3	41.1	39.8	40.4	45.3	43.2

[0082] As is shown in Table 5, in the case where the bulk density is more than 0.5 g/ml, a small particle diameter involves enlarging the surface area, therefore resulting in a fast absorption rate (high absorption capacity in a short period of time), but rather lowering the saturated absorption capacity value (absorption capacity in 20 hours). On the other hand, in the case where the bulk density is not more than 0.5 g/ml, the absorption rate is fast (the absorption capacity in a short period of time is high), and further, the saturated absorption capacity value (absorption capacity in 20 hours) is high. It is inferred that the reason why the absorption rate is fast is because the internal surface area is large, and that the reason why the saturated absorption capacity value is high is because the liquid permeability in the initial stage of the water absorption is high. (EXAMPLES 8 to 11):

[0083] The cationic crosslinked polymer particles (A1) and (A2) having particle diameters of not larger than 850  $\mu$ m were dry-blended in an amount of 100 weight parts respectively with 100 weight parts of anionic crosslinked polymer particles (B1) and (B3) (having particle diameters of not larger than 850  $\mu$ m) respectively, thus obtaining 200 weight parts of particulate water-swella-ble crosslinked polymer compositions (15) to (18) respectively. Their absorption capacities for a salt water (1,000 g in total weight as prepared by adding deionized water (solvent) to 2.0 g of potassium chloride, 2.0 g of sodium sulfate, 0.85 g of ammonium dihydrogen phosphate, 0.15 g of diammonium hydrogen phosphate, 0.25 g of calcium chloride dihydrate, and 0.5 g of magnesium chloride hexahydrate) under load in 4 hours and in 20 hours are shown in Table 6.

(COMPARATIVE EXAMPLES 8 and 9):

[0084] The cationic crosslinked polymer particles (A5) having particle diameters of not larger than 850  $\mu$ m were dry-blended in an amount of 100 weight parts with 100 weight parts of anionic crosslinked polymer particles (B1) and (B3) (having particle diameters of not larger than 850  $\mu$ m) respectively, thus obtaining 200 weight parts of particulate water-swella-ble crosslinked polymer compositions (19) and (20) respectively. Their absorption capacities for a salt water (1,000 g in total weight as prepared by adding deionized water (solvent) to 2.0 g of potassium chloride, 2.0 g of sodium sulfate, 0.85 g of ammonium dihydrogen phosphate, 0.15 g of diammonium hydrogen phosphate, 0.25 g of calcium chloride dihydrate, and 0.5 g of magnesium chloride hexahydrate) under load in 4 hours and in 20 hours are shown in Table 6.

Table6

50	Water-swella-blecrosslinked polymercomposition	Cationic crosslinked polymerparticles	Anionic crosslinked polymerparticles	Bulk density (g/ml)	Absorption capacity (g/g) underload	
					4hours	20hours
55	Example 8 (15)	(A1)	(B1)	0.383	42.5	46.0
	Example 9 (16)	(A1)	(B3)	0.399	42.1	45.2

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Table6(continued)

	Water-swella- blecrosslinked polymercom- position	Cationic crosslinked polymerparti- cles	Anionic crosslinked polymerparti- cles	Bulkdensity (g/ml)	Absorptioncapacity(g/g) underload	
					4hours	20hours
Example10	(17)	(A2)	(B1)	0.373	41.4	44.6
Example11	(18)	(A2)	(B3)	0.365	40.0	43.1
Comparative Example8	(19)	(A5)	(B1)	0.621	29.0	34.4
Comparative Example9	(20)	(A5)	(B3)	0.611	37.6	42.0

[0085] As is shown in Table 6, the absorption capacities under load in 4 hours and in 20 hours are higher in Examples 8 to 11 in which cationic crosslinked polymer having a bulk density of not more than 0.5g/ml were used than in Comparative Examples 8 and 9 in which anionic crosslinked polymer having a bulk density of more than 0.5g/ml was used. That the absorption capacity under load in 4 hours is high means that the salt water absorption rate is fast. The absorption capacity under load in 20 hours indicates almost the saturated value, therefore that this high means that the saturated absorption capacity value (absorption quantity) under load is high.

(EXAMPLES 12 and 13):

[0086] The cationic crosslinked polymer particles (A1) and (A3) having particle diameters of not larger than 850  $\mu\text{m}$  were dry-blended in an amount of 40 weight parts respectively with 60 weight parts of anionic crosslinked polymer particles (B3) (having particle diameters of not larger than 850  $\mu\text{m}$ ), thus obtaining 100 weight parts of particulate water-swella-ble crosslinked polymer compositions (21) and (22) respectively. Their absorption capacities for a salt water (1,000g in total weight as prepared by adding deionized water (solvent) to 2.0g of potassium chloride, 2.0g of sodium sulfate, 0.85g of ammonium dihydrogen phosphate, 0.15g of diammonium hydrogen phosphate, 0.25g of calcium chloride dihydrate, and 0.5g of magnesium chloride hexahydrate) under load in 4 hours and in 20 hours are shown in Table 7.

(COMPARATIVE EXAMPLE 10):

[0087] The cationic crosslinked polymer particles (A5) having particle diameters of not larger than 850  $\mu\text{m}$  were dry-blended in an amount of 40 weight parts with 60 weight parts of anionic crosslinked polymer particles (B3) (having particle diameters of not larger than 850  $\mu\text{m}$ ), thus obtaining 100 weight parts of particulate water-swella-ble crosslinked polymer composition (23). Their absorption capacities for a salt water (1,000g in total weight as prepared by adding deionized water (solvent) to 2.0g of potassium chloride, 2.0g of sodium sulfate, 0.85g of ammonium dihydrogen phosphate, 0.15g of diammonium hydrogen phosphate, 0.25g of calcium chloride dihydrate, and 0.5g of magnesium chloride hexahydrate) under load in 4 hours and in 20 hours are shown in Table 7.

Table7

	Water-swella- blecrosslinked polymercom- position	Cationic crosslinked polymerparti- cles	Anionic crosslinked polymerparti- cles	Bulkdensity (g/ml)	Absorptioncapacity(g/g) underload	
					4hours	20hours
Example12	(21)	(A1)	(B3)	0.431	40.5	44.2
Example13	(22)	(A3)	(B3)	0.433	40.7	44.5
Comparative Example10	(23)	(A5)	(B3)	0.623	37.1	41.3

[0088] As is shown in Table 7, the absorption capacities under load in 4 hours and in 20 hours are higher in Examples 12 and 13 in which a cationic crosslinked polymer having a bulk density of not more than 0.5g/ml were used than in Comparative Example 10 in which a cationic crosslinked polymer having a bulk density of more than 0.5g/ml was used. That the absorption capacity under load in 4 hours is high means that the salt water absorption rate is fast. The absorption capacity under load in 20 hours indicates almost the saturated value, therefore that this is high means that the saturated absorption capacity value (absorption quantity) under load is high.

(REFERENTIAL EXAMPLE C-1):

[0089] An aqueous monomer solution was prepared by dissolving 270g of acrylic acid, 0.4g of N,N'-methylenebisacrylamide, 0.547g of sodium persulfate, and 0.157g of 2-hydroxy-2-methylpropylphenone into 810g of deionized water, and then degassed by blowing nitrogen in for 15 minutes. This aqueous monomer solution was poured into a shallow glass dish, and then irradiated with ultraviolet rays of 15mW/cm<sup>2</sup> for 25 minutes to carry out polymerization, thus obtaining a crosslinked polyacrylic acid gel.

(COMPARATIVE EXAMPLE 11):

[0090] Ethyleneglycoldiglycidylether (trade name: "Denacol EX-810," produced by Nagase Chemicals, Ltd.) was added, in the ratio of 1.5mol% to an aqueous polyethyleneimine solution (trade name: "EPOMINP-1000," produced by Nippon Shokubai Co., Ltd.), as diluted to 10%, to carry out a reaction at 60 °C for 16 hours, thus obtaining a crosslinked polyethyleneimine gel. Then, 37.4 parts (in terms of solid content) of the resultant crosslinked polyethyleneimine gel and 62.6 parts (in terms of solid content) of the crosslinked polyacrylic acid gel, as obtained in Referential Example C-1, were separately pulverized into fine pieces in extruders, and then mixed. The resultant mixture was caused to twice pass through a meat chopper, thus obtaining a kneaded product in which both gels were uniformly kneaded and the soft gels were co-formed into a microdomain. The resultant kneaded product was dried at 60 °C in an oven for 16 hours. Inorganic fine particles (trade name: "Aerosil A-200," produced by Nippon Aerosil Co., Ltd.) were added to the resultant dried product in the ratio of 0.5% (relative to the dried product), and the resultant mixture was freeze-dried to separate particles of 85 to 150 μm, thus obtaining a water-swella ble crosslinked polymer composition (24).

[0091] This composition had a bulk density of 0.55g/ml and exhibited a desalting amount of 0.29g/g, and further exhibited absorption capacities of 18.9g/g, 25.6g/g, and 29.6g/g under load (under a load of 50g/cm<sup>2</sup>) in 1 hour, in 4 hours, and in 20 hours respectively.

(COMPARATIVE EXAMPLE 12):

[0092] Ethyleneglycoldiglycidylether (trade name: "Denacol EX-810," produced by Nagase Chemicals, Ltd.) was added, in the ratio of 1.0mol% to an aqueous polyethyleneimine solution (trade name: "EPOMINP-1000," produced by Nippon Shokubai Co., Ltd.), as diluted to 20%, to carry out a reaction at 60 °C for 16 hours, thus obtaining a crosslinked polyethyleneimine gel. Then, 37.4 parts (in terms of solid content) of the resultant crosslinked polyethyleneimine gel and 62.6 parts (in terms of solid content) of the crosslinked polyacrylic acid gel, as obtained in Referential Example C-1, were separately pulverized into fine pieces in extruders, and then mixed. The resultant mixture was caused to twice pass through a meat chopper, thus obtaining a kneaded product in which both gels were uniformly kneaded and the soft gels were co-formed into a microdomain. The resultant kneaded product was dried at 60 °C in an oven for 16 hours. Inorganic fine particles (trade name: "Aerosil A-200," produced by Nippon Aerosil Co., Ltd.) were added to the resultant dried product in the ratio of 0.5% (relative to the dried product), and the resultant mixture was freeze-dried to separate particles of 85 to 150 μm, thus obtaining a water-swella ble crosslinked polymer composition (25).

[0093] This composition had a bulk density of 0.53g/ml and exhibited a desalting amount of 0.29g/g, and further exhibited absorption capacities of 25.8g/g, 31.5g/g, and 31.3g/g under load (under a load of 50g/cm<sup>2</sup>) in 1 hour, in 4 hours, and in 20 hours respectively.

(EXAMPLE 14):

[0094] The particulate water-swella ble crosslinked polymer composition (21), as obtained in Example 12, had a bulk density of 0.431g/ml and exhibited a desalting amount of 0.41g/g, and further exhibited absorption capacities of 33.5g/g, 40.5g/g, and 44.2g/g under load (under a load of 50g/cm<sup>2</sup>) in 1 hour, in 4 hours, and in 20 hours respectively.

[0095] As is clear from the comparison of Comparative Examples 11 and 12 with Example 14, the water-swella ble crosslinked polymer composition according to the present invention, as obtained by dry-blending, exhibited a more excellent value in respect to each of the desalting amount and the absorption capacity under load than the compositions in which a microdomain was formed.

(EXAMPLE15):

[0096] First, 1,000g of a 50 weight % aqueous polyethylenimine solution (weight-average molecular weight: about 70,000, aqueous solution viscosity: about 17,000 mPa s, trade name: Epomin P-1050, produced by Nippon Shokubai Co., Ltd.) was placed into a beaker of 2 liters. Next, while being whipped, this aqueous polymer solution was stirred until it became clouded. Thereafter, 50 g of ethylene glycol diglycidyl ether (trade name: Denacol EX-810, produced by Nagase Chemicals, Ltd.) (crosslinking agent) was added thereto to mix them until a homogeneous solution was formed. The resultant mixed solution was placed into an incubator of 60 °C to carry out a crosslinking reaction. As a result, gelation began after about 1 minute, and the aqueous solution became solidified after 5 minutes. Then, after 1 hour, the resultant solid was got out and then cooled to examine its volume. Its results showed that the volume had increased by 0.6% of the volume of the original solution due to bubbles-containing. Then, the resultant lumped gel was got out, and then pulverized with a laboratory pulverizer into particle diameters of not larger than 850 μm, and then dried with a dry-goven of 60 °C for 2 hours. Then, 1.5 g of inorganic fine particles (trade name: Aerosil R972, produced by Nippon Aerosil Co., Ltd.) were added to the resultant dried particles, and the resultant blend was pulverized with a laboratory pulverizer, thus obtaining water-swella ble crosslinked polymer particles (A6) having particle diameters of not larger than 850 μm. The water-swella ble crosslinked polymer particles (A6) exhibited an absorption capacity of 6.2 g/g for physiological saline solution without load and had a bulk density of 0.287 g/ml.

(EXAMPLE16):

[0097] First, 1,000 g of polyethylenimine (weight-average molecular weight: about 10,000, viscosity: about 20,000 mPa s, trade name: Epomin SP-200, produced by Nippon Shokubai Co., Ltd.) of 40 °C was placed into a beaker of 2 liters. Next, while being whipped, this polymer was stirred until it became clouded. Thereafter, 100 g of ethylene glycol diglycidyl ether (trade name: Denacol EX-810, produced by Nagase Chemicals, Ltd.) (crosslinking agent) was added thereto to mix them until a homogeneous mixture was formed. The resultant mixture was placed into an incubator of 60 °C to carry out a crosslinking reaction. As a result, gelation began after about 2 minutes, and the reaction mixture became solidified after 6 minutes. Then, after 1 hour, the resultant solid was got out and then cooled to examine its volume. Its results showed that the volume had increased by about 1.1% of the volume of the original mixture due to bubbles-containing. Then, the resultant lumped gel was got out, and then pulverized with a laboratory pulverizer into particle diameters of not larger than 850 μm, and then to 3 g of inorganic fine particles (trade name: Aerosil R972, produced by Nippon Aerosil Co., Ltd.) were added, and the resultant blend was pulverized with a laboratory pulverizer, thus obtaining water-swella ble crosslinked polymer particles (A7) having particle diameters of not larger than 850 μm. The water-swella ble crosslinked polymer particles (A7) exhibited an absorption capacity of 6.1 g/g for physiological saline solution without load and had a bulk density of 0.254 g/ml.

(EXAMPLE17):

[0098] First, a mixture of polyethylenimine and a crosslinking agent was prepared in the same way as of Example 16 except that the crosslinking agent was changed to 75 g of acrylic acid. Next, the resultant mixture was placed into an incubator of 160 °C to carry out a crosslinking reaction. As a result, gelation began after about 20 minutes, and the reaction mixture became solidified after 30 minutes. Then, after 1 hour, the resultant lumped gel was got out, and then pulverized with a laboratory pulverizer into particle diameters of not larger than 850 μm, and then to 3 g of inorganic fine particles (trade name: Aerosil R972, produced by Nippon Aerosil Co., Ltd.) were added, and the resultant blend was pulverized with a laboratory pulverizer, thus obtaining water-swella ble crosslinked polymer particles (A8) having particle diameters of not larger than 850 μm. The water-swella ble crosslinked polymer particles (A8) exhibited an absorption capacity of 5.2 g/g for physiological saline solution without load and had a bulk density of 0.272 g/ml.

(EXAMPLE18):

[0099] Mixing of the crosslinking agent was carried out in the same way as of Example 16, and then the resultant mixture was placed into a vacuum oven of 60 °C to carry out a crosslinking reaction while the bubbles in the mixture were expanded under a vacuum of 200 to 0.1 mmHg. As a result, gelation began after about 2 minutes, and the reaction mixture became solidified after 6 minutes. Then, after 1 hour, the resultant solid was got out and then cooled to examine its volume. Its results showed that the volume had increased by about 200% of the volume of the original mixture due to bubbles-containing. Then, the resultant lumped gel was got out, and then pulverized with a laboratory pulverizer into particle diameters of not larger than 850 μm, and then to 3 g of inorganic fine particles (trade name: Aerosil R972, produced by Nippon Aerosil Co., Ltd.) were added, and the resultant blend was pulverized with a laboratory pulverizer, thus obtaining water-swella ble crosslinked polymer particles (A9) having particle diameters of not larger than 850 μm. The

water-swellaable crosslinked polymer particles (A9) exhibited an absorption capacity of 7.7 g/g for physiological saline solution without load and had a bulk density of 0.211 g/ml.

(EXAMPLES 19 to 22) (acid-base mixed composition):

**[0100]** The cationic water-swellaable crosslinked polymer particles (A6) to (A9) having particle diameters in the range of 500 to 300  $\mu\text{m}$  were dry-blended in an amount of 100 weight parts respectively with 100 weight parts of anionic water-swellaable crosslinked polymer particles (B2) having particle diameters of not larger than 850  $\mu\text{m}$ , thus obtaining 200 weight parts of particulate water-swellaable crosslinked polymer compositions (24) to (27) respectively. Their absorption capacities for salt water (1,000 g in total weight) as prepared by adding deionized water (solvent) to 2.0 g of potassium chloride, 2.0 g of sodium sulfate, 0.85 g of ammonium dihydrogen phosphate, 0.15 g of diammonium hydrogen phosphate, 0.25 g of calcium chloride dihydrate, and 0.5 g of magnesium chloride hexahydrate) under load in 4 hours and in 20 hours are shown in Table 8.

Table 8

	Water-swella- ble crosslinked polymer com- position	Cationic crosslinked polymer parti- cles	Anionic crosslinked pol- ymer particles	Bulk density (g/ml)	Absorption capacity (g/g) under load	
					4 hours	20 hours
Example 19	(24)	(A6)	(B2)	0.383	41.2	47.5
Example 20	(25)	(A7)	(B2)	0.389	41	45.2
Example 21	(26)	(A8)	(B2)	0.412	40.3	44.2
Example 22	(27)	(A9)	(B2)	0.352	40.5	42.3

**[0101]** Various details of the invention may be changed without departing from its spirit and not its scope. Furthermore, the foregoing description of the preferred embodiments according to the present invention is provided for the purpose of illustration only, and not for the purpose of limiting the invention as defined by the appended claims and their equivalents.

#### Claims

1. A water-swellaable crosslinked polymer composition, which is particulate and comprises an anionic crosslinked polymer and a cationic crosslinked polymer, with the water-swellaable crosslinked polymer composition being characterized by having a bulk density of not more than 0.5 g/ml.
2. A water-swellaable crosslinked polymer composition, which is particulate and comprises an anionic crosslinked polymer and a cationic crosslinked polymer, with the water-swellaable crosslinked polymer composition being characterized in that at least either one of the anionic crosslinked polymer and the cationic crosslinked polymer has a bulk density of not more than 0.5 g/ml.
3. A water-swellaable crosslinked polymer composition according to claim 1 or 2, wherein 50 to 100 mol % of acid groups which are contained in functional groups in the anionic crosslinked polymer are unneutralized acid groups, and wherein 50 to 100 mol % of basic groups which are contained in functional groups in the cationic crosslinked polymer are unneutralized basic groups.
4. A water-swellaable crosslinked polymer composition according to any one of claims 1 to 3, wherein the cationic crosslinked polymer is a crosslinked polymer of polyethylenimine.
5. A water-swellaable crosslinked polymer composition according to claim 4, wherein the crosslinked polymer of polyethylenimine is a crosslinked polymer which is a product by a process including the step of crosslinking a polymer of polyethylenimine having a solid content of not less than 80 weight %.
6. A water-swellaable crosslinked polymer composition according to any one of claims 1 to 5, which is a product by a

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process including the step of dry-blending an anionic crosslinked polymer having a solid content of more than 80 weight% and a cationic crosslinked polymer having a solid content of more than 80 weight%.

7. A water-swellaible crosslinked polymer composition according to any one of claims 1 to 6, wherein the cationic crosslinked polymer is a product by a process including the step of carrying out a reaction between a water-soluble polymer and a crosslinking agent under bubbles-containing conditions.
8. A particulate cationic crosslinked polymer, which has a bulk density of not more than 0.5 g/ml and exhibits an absorption capacity of at least 5 g/g for physiological saline solution without load.
9. A particulate cationic crosslinked polymer according to claim 8, wherein the cationic crosslinked polymer is a crosslinked polymer of polyethylenimine.
10. A production process for a water-swellaible crosslinked polymer, which comprises the step of carrying out a crosslinking reaction of a solution under bubbles-containing conditions wherein the solution contains at least a water-soluble polymer and a crosslinking agent.
11. A production process according to claim 10, wherein the water-soluble polymer is a polyamine.
12. A production process for a water-swellaible crosslinked polymer composition, which comprises the steps of: carrying out a crosslinking reaction of a solution under bubbles-containing conditions to obtain a cationic crosslinked polymer wherein the solution contains at least a polyamine and a crosslinking agent; and then mixing the resultant cationic crosslinked polymer and an anionic crosslinked polymer together.
13. An absorbent articles, which comprises an absorbent layer, a sheet with liquid permeability, and a sheet with liquid impermeability, wherein the absorbent layer contains the water-swellaible crosslinked polymer composition as recited in any one of claims 1 to 7, and is interposed between the sheet with liquid permeability and the sheet with liquid impermeability.

Fig. 1

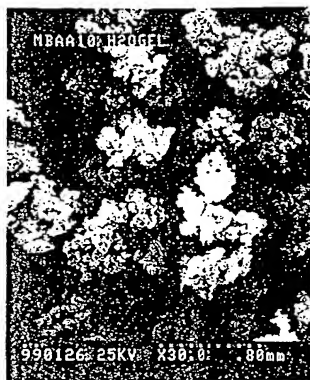


Fig. 2

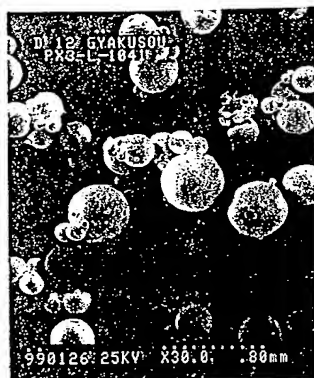
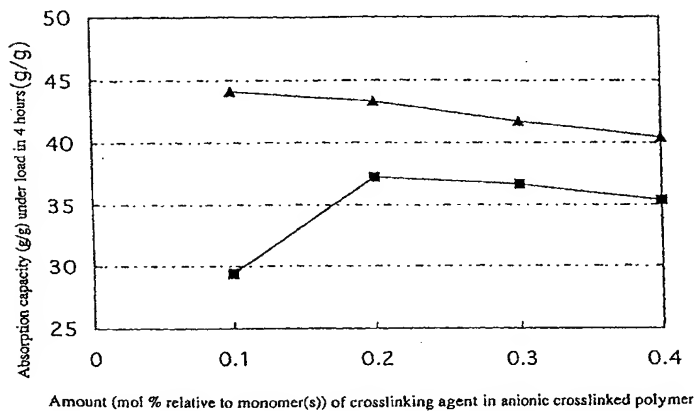


Fig. 3

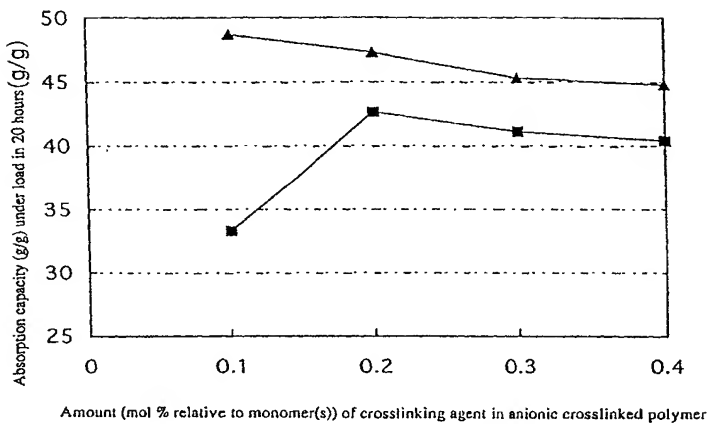


Examples 1 to 4 (water-swellaible crosslinked polymer compositions (1) to (4))

Comparative Examples 1 to 4 (water-swellaible crosslinked polymer compositions (5) to (8))



Fig. 4



Examples 1 to 4 (water-swellaible crosslinked polymer compositions (1) to (4))

Comparative Examples 1 to 4 (water-swellaible crosslinked polymer compositions (5) to (8))